Catalytic Pyrolysis of Waste Chicken Fats Using Zeolite Catalysts

M. Y. Liew, A. Salmiaton, W. A. K. G. Wan Azlina and R. Yunus

Abstract Chicken fats become a major poultry waste from broiler industries and the production rate is increasing with increasing of human population. The conversion of waste chicken fats containing major triglycerides into potential hydrocarbon chemicals and bio-oils was investigated under pyrolysis process. Catalytic pyrolysis of chicken fats with zeolite catalyst, ZSM-5, was conducted using laboratory-scale distillation set-up under nitrogen flow of 400 °C. In the process, thermal cracking plays an important role in breaking triglyceride into shorter hydrocarbon chain under high temperature. Pyro-oil produced was further analysed by gas chromatography–mass spectroscopy in order to identify its chemical properties. From the chemical analysis, different short hydrocarbon chain products from C_7–C_{24} were indicated. Major chemical composition of pyro-oil ascertained was aliphatics, followed by carboxylic acid, alcohol, ketone, ester, aromatic, anhydride, ether and aldehyde. The effect of ZSM-5 catalysts towards product yield and composition was also explored.

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Introduction

Fossil fuels represent more than 80 % of total energy in the world and act as the primary resource nowadays. But the scarcity of this conventional energy has become a problem due to the rising of energy demand (Demirbas 2008). The application of renewable energy from biomass conversion via chemical process can be a potential new energy resource. Pyrolysis is a process of thermal decomposition of materials at high temperatures with the absence of oxygen (Jayasinghe and Hawboldt 2012). The production of bio-oil from pyrolysis involves rapid heating to breakdown long hydrocarbon chain species producing smaller hydrocarbon products that have similar fuel properties.

Bio-oil derived from animal fats such as lard, poultry fats and fish oil showed diesel-like fuel properties with major components of alkanes, alkenes, aldehydes, ketones, aromatics and carboxylic acids (Adebanjo et al. 2005; Tian et al. 2008; Wisniewski Jr et al. 2010). Gürü et al. (2010) investigated the performance and emission characteristics of bio-oil on running engines and compared to those of fossil fuel and fatty acid methyl esters. The authors found that bio-oil with low sulphur content was performed well with diesel fuel blends.

Catalytic pyrolysis is a more advanced technique to maximise the production of pyrolytic products and increase the selectivity on specific compositions of compounds (Butler et al. 2011). In one research conducted by Carlson et al. (2009), ZSM-5 catalyst showed good performance in producing higher aromatic compounds. Higher aromatics improved the properties of higher heating value due to relatively reduced oxygenated compounds.

Methodology

Materials

Waste chicken fats as raw materials were collected from a public market located at Seri Kembangan, Selangor for torrefaction. The chicken fats stripped off directly from different chicken species were stored in a fridge of 4 °C after collected. Torrefaction of chicken fats was carried out in a reflux set-up at 200 °C under 300 ml/min of nitrogen flow rate in order to create an oxygen-free condition. About 80 % of torrefied biomass was extracted and was prepared for pyrolysis.

Ultimate analysis of torrefied biomass was performed by LECO CHNS-932 elemental analyser as shown in Table 1. Higher heating value (HHV) was theoretically calculated according to Dulong's formula using the percentage of C, H, O and S elements from the analysis (Rajput 2010).

ZSM-5 catalyst used was a commercialised catalyst purchased from Qingdao Wish Chemical Co., Ltd. It was synthesised from water glass and aluminium

Table 1 Ultimate analysis of torrefied biomass

Ultimate analysis (wt% daf)				
C	H	N	S	O*
77.21	11.96	0.84	0.28	9.71
Heating value (HHV, MJ/kg)			41.64	

*By difference

sulphate and suitable employed in the production oil catalytic cracking reaction (den Hollander et al. 2002).

Pyrolysis of Torrefied Biomass

The torrefied biomass was pyrolysed in a distillation set-up with heat source supplied from heating mantle, nitrogen gas connection and thermocouple. The nitrogen gas was pre-purged for 15 min with 300 ml/min of nitrogen flow rate to create oxygen-free environment prior to pyrolysis process. Non-catalytic and catalytic pyrolysis using ZSM-5 catalyst were conducted in the same pyrolysis condition to investigate the effectiveness of the catalyst. The condition was set at temperature of 400 °C for 30 min under 300 ml/min nitrogen flow rate and 350 rpm stirring rate.

GC–MS and FTIR Analysis

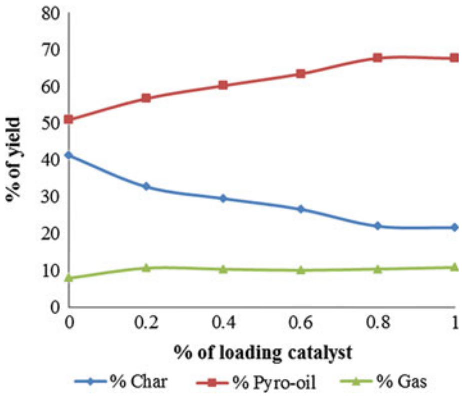
Chemical properties of pyro-oil produced were analysed using gas chromatography-mass spectroscopy (GC–MS, Shimadzu GCMS-QP2010 Plus). A capillary column SGE BPX5 (length 30 m, ID 0.25 mm and film thickness 0.25 μm) was used in the GC analysis. Helium gas was employed as a carrier gas at 1.0 ml/min with a pressure set at 53.6 kPa. Injector and interface temperature were operated at 250 and 320 °C, respectively. Injection volume of pyro-oil was 0.1 μl in split mode ratio of 1:50. Oven temperature was pre-run at 50 °C for 2 min, increased to 300 °C at heating rate of 8 °C/min and maintained for 10 min.

Results and Discussion

Product Yield

The products obtained from pyrolysis of torrefied biomass were divided into three fractions namely char, pyro-oil and gas (calculated by difference). Figure 1 portrayed the product yield of catalytic pyrolysis of waste chicken fats.

Fig. 1 Yields of catalytic pyrolysis at different percentage of loading catalyst



The effectiveness of ZSM-5 towards yield production was determined by different percentage of catalyst loading to the torrefied biomass mixture pyrolysed at 400 °C. The pyro-oil yield was increased from 50.92 to 67.60 % as the catalyst loading increased from 0.2 to 1.0 %. It was observed that the yield of char decreased from 41.19 to 21.61 % and the gas production was slightly increased from 7.89 to 10.79 % with the increase in catalyst loading. The maximum yield of pyro-oil was occurred when the biomass was pyrolysed with 0.8 % ZSM-5 catalyst, and the yield was slightly reduced with 1.0 % catalyst loading. It can be explained that at the condition above optimum, pyrolysis was more favoured to gasification reaction when higher amount of catalyst was employed (Pütün et al. 2006; Pütün 2010).

Pyro-Oil Characterisation

Various compositions of pyro-oils were observed in the GC–MS analysis and their chromatograms were shown in Fig. 2. Different compositions of non-catalytic pyro-oil and ZSM-5 catalytic pyro-oil were grouped based on carbon numbers and chemical groups in order to determine thermal cracking of hydrocarbon and the selectivity of catalyst (Pütün et al. 2006). Both pyro-oil contained a series of organic compounds with carbon number from C_7 to C_{24} (Fig. 3a). The most abundant compound for both was aliphatic in C_{15}, distributed around 21.59 and 23.11 %, respectively. Catalytic pyro-oil showed higher diversity in C_7–C_{15} (67.12 %) than non-catalytic pyro-oil (61.84 %) due to efficient of catalyst in thermal degradation of higher hydrocarbon into smaller product (Butler et al. 2011). C_{16} and C_{17} products from non-catalytic pyro-oil were significantly reduced from 7.64 to 1.93 % and 15.7 to 5.86 % after the loading of ZSM-5 catalyst, respectively.

Different kinds of compounds were classified based on chemical group (Fig. 3b). The main group for both pyro-oil was aliphatic, followed by carboxylic acid and alcohol with some in ketone and ester and traces in aromatic, anhydride,

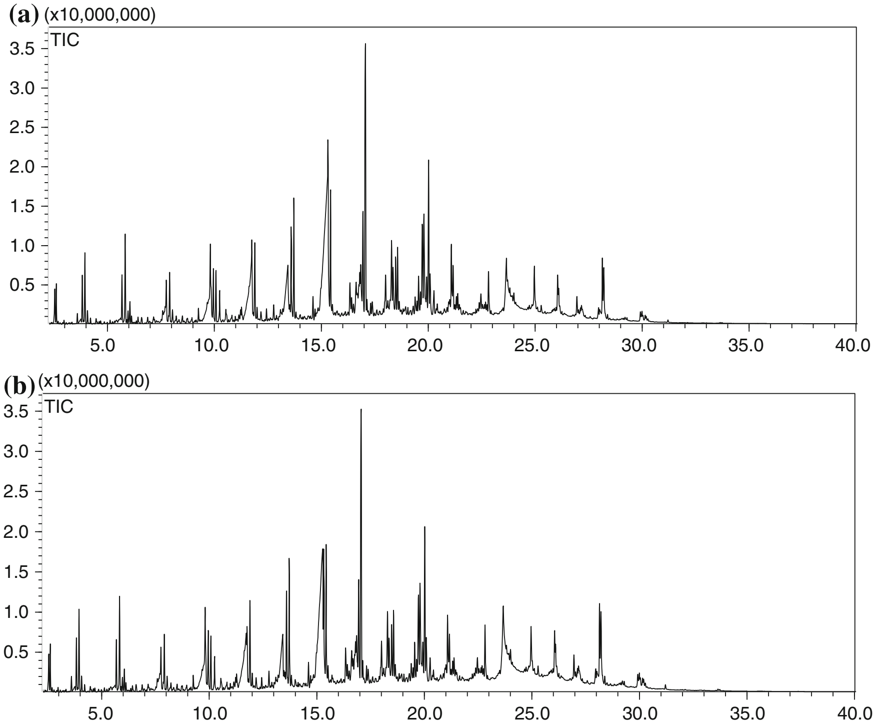


Fig. 2 GC–MS Chromatograms of **a** non-catalytic pyro-oil and **b** ZSM-5 catalytic pyro-oil

ether and aldehyde. Catalytic pyro-oil showed high selectivity in aliphatic compounds as its distribution increased from 55.34 % (non-catalytic pyrolysis) to 61.00 % (catalytic pyrolysis). As reported by Pütün et al. (2006), the advantage of zeolite catalyst was apparently improved the yield of aliphatic fraction. ZSM-5 catalytic pyrolysis favoured the production of alcohols as well, from 9.50 % (non-catalytic pyrolysis) increased to 12.15 % (catalytic pyrolysis). Other than aliphatic and alcohol groups, catalytic pyrolysis was selectively performed on other minor components (anhydrides, aromatics, ester and ketones) with slight increment from 0.05 to 1.11 %. But, ZSM-5 catalyst was not selective in production of carboxylic acids (the second major component) and its yield was decreased from 32.13 to 21.71 %.

Conclusions

Catalytic pyrolysis of torrefied chicken fats using ZSM-5 catalysts showed an increase in pyro-oil and gas production while decrease in char production. The maximum pyro-oil yield was 32.89 % at 0.8 % catalysts loading. From the

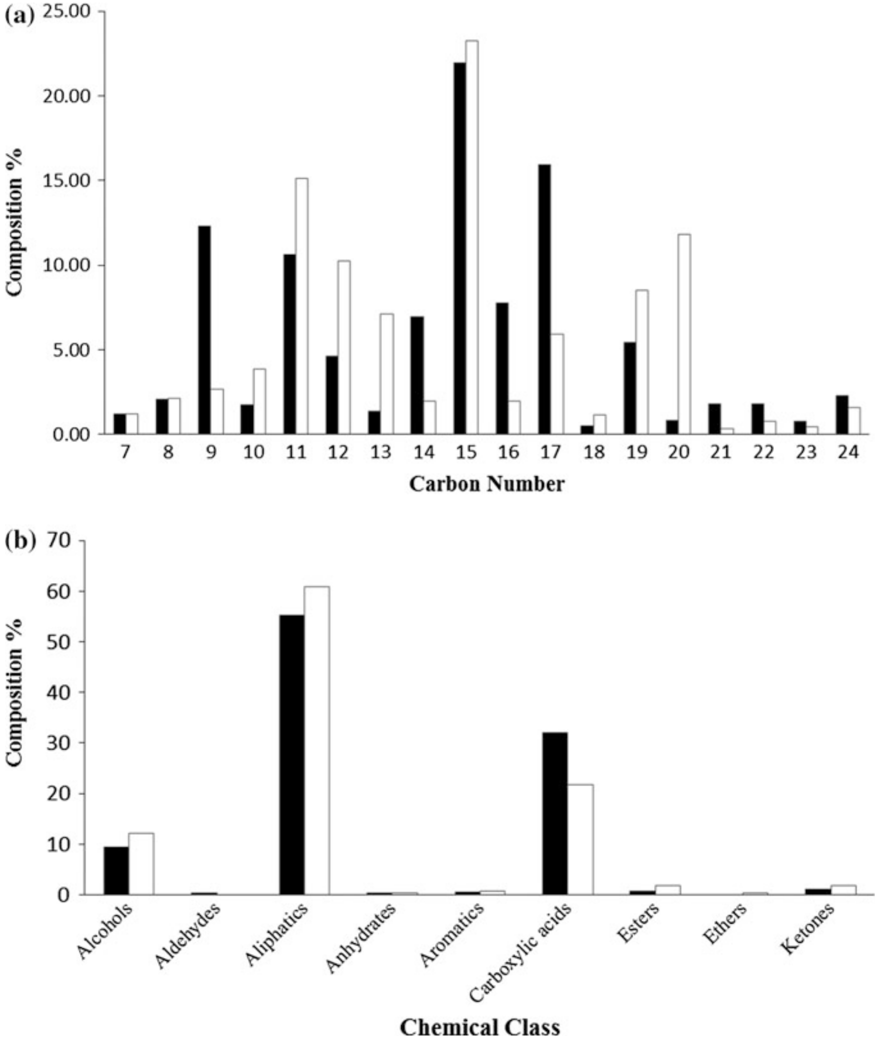


Fig. 3 Composition distribution of **a** carbon number and **b** chemical group for non-catalytic pyro-oil (*black bar*) and ZSM-5 catalytic pyro-oil (*white bar*)

GC–MS analysis, different kinds of organic compounds from carbon number C_7–C_{24} were found. Aliphatic C_{15} for non-catalytic pyro-oil and catalytic pyro-oil was dominant among other compounds. By comparison, catalytic pyro-oil had higher selectivity in chemical group of alcohols, aliphatics, anhydrides, aromatics, ester and ketones.

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References

Adebanjo, A. O., Dalai, A. K., & Bakhshi, N. N. (2005). Production of diesel-like fuel and other value-added chemicals from pyrolysis of animal fat. *Energy and Fuels, 19*, 1735–1741.

Butler, E., Devlin, G., Meier, D., & Mcdonnell, K. (2011). A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading. *Renewable and Sustainable Energy Reviews, 15*, 4171–4186.

Carlson, T., Tompsett, G., Conner, W., & Huber, G. (2009). Aromatic production from catalytic fast pyrolysis of biomass-derived feedstocks. *Topics in Catalysis, 52*, 241–252.

Demirbas, A. (2008). *Biodiesel: A realistic fuel alternative for diesel engines*. London: Springer.

Den Hollander, M. A., Wissink, M., Makkee, M., & Moulijn, J. A. (2002). Gasoline conversion: Reactivity towards cracking with equilibrated FCC and ZSM-5 catalysts. *Applied Catalysis, A: General, 223*, 85–102.

Gürü, M., Koca, A., Can, Ö., Çinar, C., & Şahin, F. (2010). Biodiesel production from waste chicken fat based sources and evaluation with Mg based additive in a diesel engine. *Renewable Energy, 35*, 637–643.

Jayasinghe, P., & Hawboldt, K. (2012). A review of bio-oils from waste biomass: Focus on fish processing waste. *Renewable and Sustainable Energy Reviews, 16*, 798–821.

Pütün, E. (2010). Catalytic pyrolysis of biomass: Effects of pyrolysis temperature, sweeping gas flow rate and MgO catalyst. *Energy, 35*, 2761–2766.

Pütün, E., Uzun, B. B., & Pütün, A. E. (2006). Fixed-bed catalytic pyrolysis of cotton-seed cake: Effects of pyrolysis temperature, natural zeolite content and sweeping gas flow rate. *Bioresource Technology, 97*, 701–710.

Rajput, R. K. (2010). *Thermal Engineering*. New Delhi: Laxmi Publications Pvt Limited.

Tian, H., Li, C., Yang, C., & Shan, H. (2008). Alternative processing technology for converting vegetable oils and animal fats to clean fuels and light olefins. *Chinese Journal of Chemical Engineering, 16*, 394–400.

Wisniewski, JR, A., Wiggers, V. R., Simionatto, E. L., Meier, H. F., Barros, A. A. C., & Madureira, L. A. S. (2010). Biofuels from waste fish oil pyrolysis: Chemical composition. Fuel, *89*, 563-568.